Dyes and Pigments 120 (2015) 314–321

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Crowning of dibenzosilole with a naphthalenediimide functional group to prepare an electron acceptor for organic solar cells

Akhil Gupta [a, *, 1], Rahul V. Hangarge [b, 1], Xizu Wang [c, 1], Ben Alford [a, 2], Vijila Chellapan [c], Lathe A. Jones [a, d, 2], Anushri Rananaware [a, 2], Ante Bilic [e], Prashant Sonar [c, f, **], Sheshanath V. Bhosale [a, *]

[a] School of Applied Sciences, RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia
[b] Department of Organic Chemistry, School of Chemical Sciences, North Maharashtra University, Jalgaon 425 001, Maharashtra, India
[c] Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Singapore
[d] Centre for Advanced Materials and Industrial Chemistry (CAMIC), RMIT University, GPO Box 2476, Melbourne, Victoria 3001, Australia
[e] CSIRO Manufacturing, Virtual Nanoscience Lab, Parkville, Victoria 3052, Australia
[f] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

ARTICLE INFO

Article history:
Received 14 January 2015
Received in revised form
21 April 2015
Accepted 22 April 2015
Available online 5 May 2015

Keywords:
Dibenzosilol
Naphthalene diimide
Solution-processable BHJ
Organic
Organic electronics
Poly(3-hexylthiophene) (P3HT)

ABSTRACT

A novel, solution-processable non-fullerene electron acceptor 9,9′-(5,5-dioctyl-5*H*-dibenzo[*b*,*d*]silole-3,7-diyl)bis(2,7-dioctyl-4-(octylamino)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone) (**B3**) based on dibenzosilole and naphthalenediimide building blocks was designed, synthesized, characterized and successfully used in a bulk-heterojunction organic solar cell. **B3** displayed excellent solubility, thermal stability and acquired electron energy levels matching with those of archetypal donor polymer poly(3-hexylthiophene). Solution-processable bulk-heterojunction devices afforded 1.16% power conversion efficiency with a high fill factor of 53%. **B3** is the first example in the literature using this design principle, where mild donor units at the peripheries of end-capped naphthalenediimide units tune solubility and optical energy levels simultaneously.

1. Introduction

Over the last decade, the development of solution-processable bulk-heterojunction (BHJ) solar cells has seen a dramatic surge due to intense research activity, resulting in increased power conversion efficiencies (PCEs) [1–5]. For most research groups, increasing the PCE has been a key aim and PCEs have increased from less than 1% in the initial reports to 10% in recent publications [6]. However, increasing efficiencies usually stem from the development of new electron donor materials that exhibit improved optoelectronic properties, such as light harvesting, and favourably tuned highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, which match with those of electron acceptors [1]. In fact, electron acceptors are materials which should be considered as equally important as donor materials. But in practice, the development of electron acceptors has trailed far behind that of donors. It is thus desirable that further research is carried out on the development of electron acceptor materials.

With regards to electron acceptor materials, conventional fullerenes and their derivatives, such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and its C_{71} analogue $PC_{71}BM$, are the most common acceptors of choice, thanks to their superior electron affinity and good electron mobility [7,8]. Despite these inherent properties, fullerene derivatives are afflicted with a number of disadvantages, such as weak absorption in the visible spectrum, restricted electronic tuning, and a large electron affinity that can result in low open-circuit voltages (V_{oc}) [9]. Hence, incentives remain to develop non-fullerene

---

* Corresponding authors. Tel.: +61 3 9925 2680.
** Corresponding author. School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia.
E-mail addresses: akhilgk15@gmail.com (A. Gupta), sonar.prashant@qut.edu.au (P. Sonar), sheshanath.bhosale@rmit.edu.au (S.V. Bhosale).
[1] These authors contributed equally to this work.
[2] Tel.: +61 3 9925 2680.

http://dx.doi.org/10.1016/j.dyepig.2015.04.033

electron acceptors that retain the favourable properties of fullerene derivatives and also overcome their insufficiencies. In order to design new acceptors, one has to consider desirable properties such as (1) strong and broad absorption, (2) high charge carrier mobility, (3) solubility and (4) appropriate energy levels. Currently, a popular strategy for tailoring the properties of electron acceptors is through assimilating electron-withdrawing building blocks which are illustrated by, but not limited to, cyano, carbonyl, amide, imide groups and their emerging analogues. Therefore, it is not surprising that there exists a growing interest for the development of small molecular non-fullerene acceptors for solution-processable BHJ devices. Key examples of this approach were recently reported by P. Sonar et al. and Y. Lin et al. [10,11].

Recently, inspired by the brisk development of electron- and hole-transporting materials for organic electronics, various research groups have begun to explore non-fullerene acceptors for solution-processable BHJ devices [12–21]. PCEs linger around 2% and 4% with the use of classical donor polymer poly(3-hexylthiophene) (P3HT) and non-P3HT donors, respectively [22–29]. This progress is promising, albeit appreciable scope still exists to develop new non-fullerene acceptors which possess strong optical absorption, good photochemical stability and adequate solubility. In line with this outlook, functionalities such as dibenzosilole (DBS) and naphthalenediimide (NDI) have shown considerable promise as versatile building blocks for the development of non-fullerene acceptors. We and others have successfully shown examples of target materials based on such building blocks [10,23,30].

In this study we have chosen the DBS and NDI functionalities to be used in conjunction to design and develop a target material that (1) possesses elongated conjugation with good structural planarity, (2) shows high chemical and thermal stability, and (3) is highly soluble in common organic solvents. Keeping in mind that solubility is a critical requirement, we further envisioned the incorporation of peripheral lipophilic chains on the terminal NDI functionalities. This was done in practice by choosing a chemical entity (–octylamine) that contains nitrogen, a conventional donor atom. The use of such donor atoms has been successful in fine tuning optical energy levels [31]. The inclusion of such extraneous chains is in addition to the conventional alkyl chains already present on the nitrogen and silicon atoms of NDI and DBS functionalities, respectively. Such a target material with eight alkyl chains (all the chains were selected to be identical (–octyl) from a molecular symmetry point of view) is a highly conjugated and well-proportioned molecule, and is highly novel on its own. The presence of these alkyl chains not only helps to enhance the solubility of target chromophore, but also demonstrates excellent film forming properties without crystallization occurring in the film. The presence of free hydrogen atoms on the terminal nitrogen atoms assists to enhance the intra- and intermolecular interactions for better π–π stacking. The target material reported herein, 9,9′-(5,5-dioctyl-5*H*-dibenzo[*b*,*d*]silole-3,7-diyl)bis(2,7-dioctyl-4(octylamino)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone),has been coded as **B3** and carries a DBS functionality at the central core with NDI units carrying peripheral chains as terminal substituents end-capped at the both ends (see Fig. 1). An initial screen of efficacy of **B3** as an *n*-type material was carried out by using it in a solution-processable BHJ device along with classical donor polymer P3HT. The BHJ device based on P3HT:**B3** (1:1 w/w) exhibited PCE as high as 1.16% with a high fill factor (FF) of 53.4%. This value of FF is amongst the top values for a small molecular non-fullerene acceptor which has been incorporated into a single-junction BHJ device without any special treatment. **B3** is the first non-fullerene electron acceptor in the literature with DBS as a core and NDI as arms. The present work is a continuation of our efforts on the design and development of small molecular chromophores for organic electronic applications [32–35].

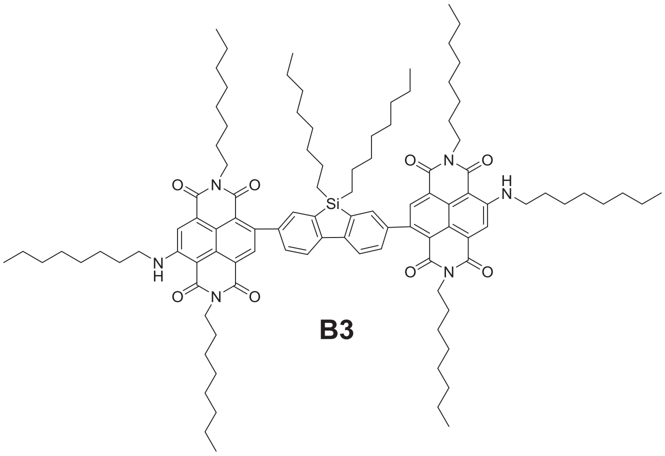

Fig. 1. Molecular structure of the newly designed and synthesized non-fullerene electron acceptor **B3**.

2. Experimental section

2.1. Materials and instruments

All the reagents and chemicals used, unless otherwise specified, were purchased from Sigma-Aldrich Co. The solvents used for synthetic reactions were obtained from Merck Speciality Chemicals (Sydney, Australia) and were used as received. 4,9-dibromo-2,7-dioctylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone was reported previously [31]. Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV400 spectrometer at 400 MHz and 100.6 MHz, respectively, or a Bruker AV200 spectrometer at 200 MHz and 50 MHz, respectively. Chemical shifts (δ) are measured in parts per million (ppm). Thin Layer Chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel, and visualised using ultraviolet (UV) light (254 nm and 365 nm). Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. High resolution mass spectra experiments were carried out on MALDI-TOF mass spectrometer. All ultraviolet–visible (UV–Vis) absorption spectra were recorded on a Hewlett Packard HP 8453 Diode array UV–Vis spectrophotometer. Thin films were spin-coated from *o*-dichlorobenzene (*o*-DCB) at a spin speed of 2000 rpm for 1 min onto cleaned glass slides. **B3** was spin-coated from solutions at a concentration of 20 mg/mL. P3HT:**B3** blend solutions were prepared in the same manner as for devices, i.e. P3HT (15 mg) and **B3** (15 mg) in a total volume of 1 mL. Where specified, films were annealed at 110 °C for 5 min. Fluorescence spectra were recorded using a Perkin–Elmer LS50B fluorimeter. Photoelectron Spectroscopy in Air (PESA) measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on clean glass substrates. The thermal stability of **B3** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Cyclic-voltammetry was performed in freshly distilled dichloromethane (over calcium hydride), with a supporting electrolyte of 0.1 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$, Electrochemical grade, Aldrich) which was twice recrystallized from ethanol before use. A Glassy carbon electrode was used as a working electrode (ALS, Japan), which was polished with 0.05 μm alumina on a felt pad, washed with distilled water followed by ethanol and dried under a N_2 stream before use. A platinum wire was used as a counter electrode and a silver wire was used as a pseudo reference electrode. Ferrocene was used as an